ULTRA-SUPERCRITICAL STEAM CORROSION

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ABSTRACT

Efficiency increases in fossil energy boilers and steam turbines are being achieved by increasing the temperature and pressure at the turbine inlets well beyond the critical point of water. To allow these increases, advanced materials are needed that are able to withstand the higher temperatures and pressures in terms of strength, creep, and oxidation resistance. As part of a larger collaborative effort, the Albany Research Center (ARC) is examining the steam-side oxidation behavior for ultra-supercritical (USC) steam turbine applications. Initial tests are being done on six alloys identified as candidates for USC steam boiler applications: ferritic alloy SAVE12, austenitic alloy Super 304H, the high Cr-high Ni alloy HR6W, and the nickel-base superalloys Inconel 617, Haynes 230, and Inconel 740. Each of these alloys has very high strength for its alloy type. Three types of experiments are planned: cyclic oxidation in air plus steam at atmospheric pressure, thermogravimetric analysis (TGA) in steam at atmospheric pressure, and exposure tests in supercritical steam up to 650ºC (1202°F) and 34.5 MPa (5000 psi). The atmospheric pressure tests, combined with supercritical exposures at 13.8, 20.7, 24.6, and 34.5 MPa (2000, 3000, 4000, and 5000 psi) should allow the determination of the effect of pressure on the oxidation process.

INTRODUCTION

Increasing the temperature and pressure in a steam turbine increases the efficiency of the Rankine steam cycle used in power generation. This has the beneficial effect of decreasing the amount of fossil fuel consumed and the emissions generated. An increase in plant efficiency from 35% to 50% is estimated to decrease CO_2 emissions by nearly 30% [Rao 2001]. Much progress has been made over the last 30 years in increasing the temperature and pressure through the development and use of high strength ferritic steels in boiler and steam turbine components.

Increased efficiencies and decreased emissions are part of three major U.S. DOE power generation initiatives: Vision 21, FutureGen, and Clean Coal Power [Dogan and Wright 2003]. For example, the

Vision 21 initiative has the goal of 50% efficiency[1] for coal-based power generation. The Clean Coal Power initiative has goals of a 675ºC (1247ºF) steam temperature by 2010 (45-50% efficiency) and 760ºC (1400ºF) by 2020 (50-60% efficiency). Currently, most supercritical boilers have steam temperatures of 565ºC (1049ºF); a few have steam temperatures of 593ºC (1099ºF) [Kishimoto *et al.* 1994].

The Advanced Research (AR) program has two efforts in ultra-supercritical (USC) steam—one on USC boilers and one on USC turbines. The overall steam temperature and pressure goal is 760ºC (1400ºF) and 38.5 MPa (5586 psi) by 2020. There are intermediate goals for demonstrating the use of materials with steam temperatures of 650ºC (1202ºF) by 2010 and 760ºC (1400ºF) by 2015 [Dogan and Wright 2003]. The Albany Research Center (ARC) is taking part in the steamside oxidation research in the USC turbine effort. A major part of the USC turbine effort is the selection or development of candidate alloys suitable for use in the USC turbine. Until candidate alloys are selected, initial tests at ARC will be done using the six candidates from the USC boiler project that have already been identified. These are ferritic alloy SAVE12, austenitic alloy Super 304H, the high Cr-high Ni alloy HR6W, and the nickel-base superalloys Inconel 617, Haynes 230, and Inconel 740. Each of these alloys has very high strength for its alloy type. Three types of oxidation experiments are planned: cyclic oxidation in air plus steam at atmospheric pressure, thermogravimetric analysis (TGA) in steam at atmospheric pressure, and exposure tests in supercritical steam up to 650°C (1202°F) and 34.5 MPa (5000 psi). This temperature and pressure correspond to the intermediate USC goal for demonstration use by 2010.

An important question to be answered is the role of pressure on steamside oxidation. It is important in two aspects. The most important one comes from that fact that most of the efficiency gains result from increased temperature, not pressure [Viswanathan and Bakker 2001]. As a consequence, material requirements, in terms of high temperature strength and steamside oxidation, could lead to the use of lower pressures (than the goal of 38.5 MPa) to make USC turbines economical, and yet still beneficial in terms of efficiency increases. The other aspect is that testing of alloys at higher temperatures and pressures than 650°C (1202°F) and 34.5 MPa (5000 psi) becomes very expensive. If the role of pressure on steamside oxidation was understood better, then less expensive tests at higher temperature and lower pressures should provide the necessary information at lower cost. The planned atmospheric pressure tests, combined with supercritical exposures at 13.8, 20.7, 24.6, and 34.5 MPa (2000, 3000, 4000, and 5000 psi), are designed to determine the effect of pressure on the oxidation process in supercritical environments.

ALLOYS

Initial oxidation experiments will be done on the six alloys selected as candidates for the USC boiler effort. The primary aim of these initial experiments is to ensure that the three types of experiments are working properly and will be ready when the USC turbine alloys are selected. However, these results should also benefit the USC boiler research and overall USC goals. The six alloys are ferritic alloy SAVE12, austenitic alloy Super 304H, the high Cr-high Ni alloy HR6W, and the nickel-base superalloys Inconel 617, Haynes 230, and Inconel 740.

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[1] Efficiency, as used here, is based on higher heating value (HHV), or gross calorific value.

Ferritic stainless steels with 9-12% Cr are currently used with steam temperatures of about 600ºC (1112ºF). Most estimates of the upper temperature limit are about 650ºC (1202ºF), with high temperature strength being the limiting factor. Two very similar alloys, SAVE12 (Sumitomo Metal Industries) and NF12 (Nippon Steel Co.), have 10^5h creep rupture strengths of 180 MPa at 600ºC (1112ºF) [Viswanathan and Bakker 2001]. The composition of SAVE12 is given in Table 1.

Table 1: Composition of ferritic stainless steel SAVE12.

	C	Si	Mn	Cr	W	Co	V	Nb	N	Ta	Nd
SAVE12	0.01	0.3	0.20	11.0	3.0	3.0	0.20	0.07	0.04	0.07	0.04

Austenitic stainless steels maintain their strength at higher temperatures than ferritic alloys, and so were used in the early USC plants in the 1950s and 1960s. However, severe thermal fatigue problems prevented their continued use at the original design temperatures and pressures. Because thermal fatigue becomes more of an issue in thicker component sections, austenitic alloys may still find use in certain thinner components. One alloy was selected as a candidate USC boiler alloy: SUPER304H. Its composition is shown in Table 2. It has a 10^5h creep rupture strength of 168 MPa at 600ºC (1112ºF) [Viswanathan and Bakker 2001]. It is currently used in boiler sections of advanced Japanese USC power stations (including Matsuura 2, Haramachi 2, Misumi 1, Tsuruga 2, Tachibanawan 2, and Isogo 1) with steam parameters as high as 28.0 MPa/605ºC/613ºC (Isogo 1) [Blum and Hald 2002].

Table 2: Composition of austenitic stainless steel SUPER304H.

	C	Si	Mn	Ni	Cr	Nb	Cu	N
SUPER304H	0.10	0.2	0.8	9.0	18.0	0.40	3.0	0.10

The high Cr-high Ni alloy HR6W is also a candidate USC boiler alloy. Its composition is shown in Table 3.

Table 3: Composition of high Cr-high Ni alloy HR6W.

	C	Si	Mn	Ni	Cr	W	Nb	Ti	B
HR6W	0.08	0.4	1.2	43.0	23.0	6.0	0.08	0.08	0.003

Three nickel-base superalloys are candidates: Inconel 617, Haynes 230, and Inconel 740. Extensive prior testing for gas turbines applications should reduce their development time and cost as compared to new superalloys. Their compositions are shown in Table 4.

Table 4: Composition of nickel-base superalloys.

	Cr	Ni	Co	Mo	W	Al	Fe	C	B	Other
Inconel 617	22.0	55.0	12.5	9.0		1.0		0.07		
Haynes 230	22.0	Bal	5.0 max	2.0	14.0	0.35	3.0 max	0.10	0.015 max	0.02 La
Inconel 740	25.0	48.3	20.0	0.5		0.9	0.7	0.03		1.8 Ti 2.0 Nb 0.30 Mn 0.5 Si

EXPERIMENTS

Three types of oxidation experiments are planned: cyclic oxidation in air plus steam at atmospheric pressure, thermogravimetric analysis (TGA) in steam at atmospheric pressure, and exposure tests in supercritical steam up to 650ºC (1202°F) and 34.5 MPa (5000 psi). The atmospheric pressure tests, combined with supercritical exposures at 13.8, 20.7, 24.6, and 34.5 MPa (2000, 3000, 4000, and 5000 psi) are designed to determine the effect of pressure on the oxidation process.

Cyclic oxidation tests will measure how the material reacts to rapid changes in temperature. In particular, differences in the thermal expansion coefficients of the base alloy and its oxide scale can lead to the spallation of the scale and possible erosion of downstream components, i.e., turbine blades and buckets. Cyclic oxidation tests will be conducted at atmospheric pressure in air at temperatures up to 800ºC (1472°F).

The apparatus is shown in Fig. 1. It consists of a vertical tube furnace fitted with an upper end cap attached to a linear slide. Seven samples can be attached to the upper end cap. The linear slide is programmed to move the samples in and out of the furnace at regular (hourly) cycles. The samples are temporarily removed and weighed at periodic intervals, then replaced in the furnace. A metering pump injects water into a heated tube to produce steam at the bottom of the furnace and create an air plus steam environment.

The TGA tests in steam provide information on the mechanism of oxidation in terms of kinetics and activation energies. The apparatus is shown in Fig. 2. A single sample is suspended from a balance into a vertical tube furnace. Steam is injected into the base of the tube furnace with a metering pump. It is condensed and collected from a side port above the furnace. A dissolved oxygen (DO) sensor measures the oxygen content of the input water. Bubbling nitrogen gas through the input water, containing a known percentage of oxygen, fixes the input water at a particular DO content.

Fig. 1: Cyclic oxidation apparatus.

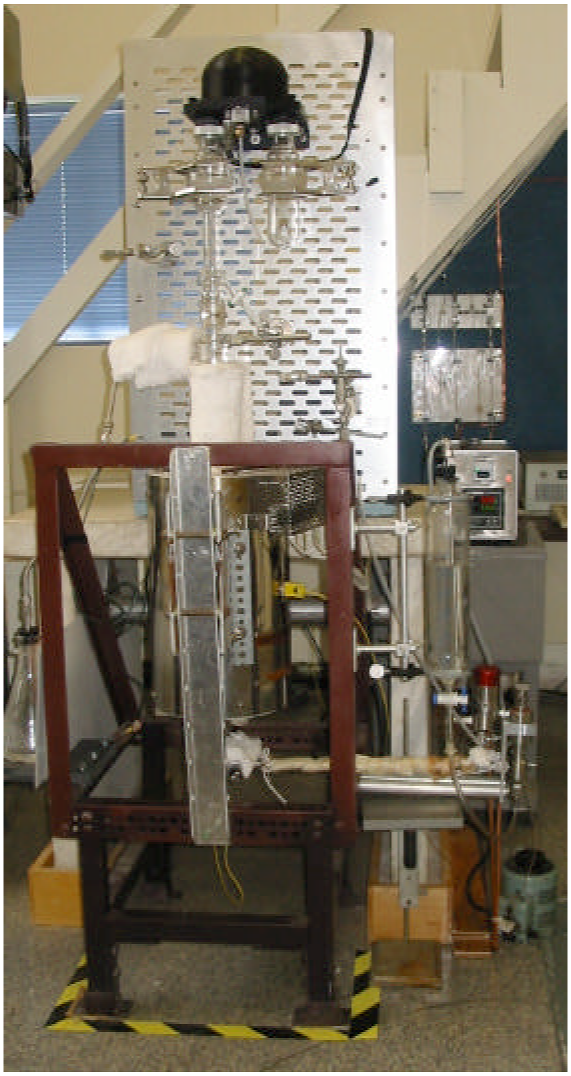

Fig. 2: TGA Apparatus.

Oxidation testing in supercritical steam at temperatures up to 650ºC (1202°F) and pressures up to 34.5 MPa (5000 psi) provides long-term exposures of candidate materials in conditions that match one of the intermediate goals of the USC project. Tests as a function of pressure at 13.8, 20.7, 24.6, and 34.5 MPa (2000, 3000, 4000, and 5000 psi), will allow the effect of pressure on oxidation to be determined in USC steam.

Construction of the apparatus has not been completed and a schematic is shown in Fig. 3. The autoclave will have a volume of 0.5 to 1.0 liter. Water will be injected with a room temperature syringe pump controlling the inlet pressure. Exit water will pass through a valve controlling the outlet flow rate. The inlet and outlet controls will maintain a constant low flow of USC steam through the autoclave where samples are exposed. The DO of the input water will be controlled and measured as in the TGA tests.

SUMMARY

The Albany Research Center (ARC) is examining the steam-side oxidation behavior for USC steam turbine applications. Increased temperatures and pressures over existing power plants will increase efficiency and decrease emissions. Initial tests are planned on six alloys identified as candidates for USC steam boiler applications: ferritic alloy SAVE12, austenitic alloy Super 304H, the high Cr-high Ni alloy HR6W, and the nickel-base superalloys Inconel 617, Haynes 230, and Inconel 740. Three types of oxidation experiments are planned: cyclic oxidation in air plus steam at atmospheric pressure, thermogravimetric analysis (TGA) in steam at atmospheric pressure, and exposure tests in supercritical steam up to 650ºC (1202°F) and 34.5 MPa (5000 psi). The atmospheric pressure tests, combined with supercritical exposures at 13.8, 20.7, 24.6, and 34.5 MPa (2000, 3000, 4000, and 5000 psi) are designed to determine the effect of pressure on the oxidation process.

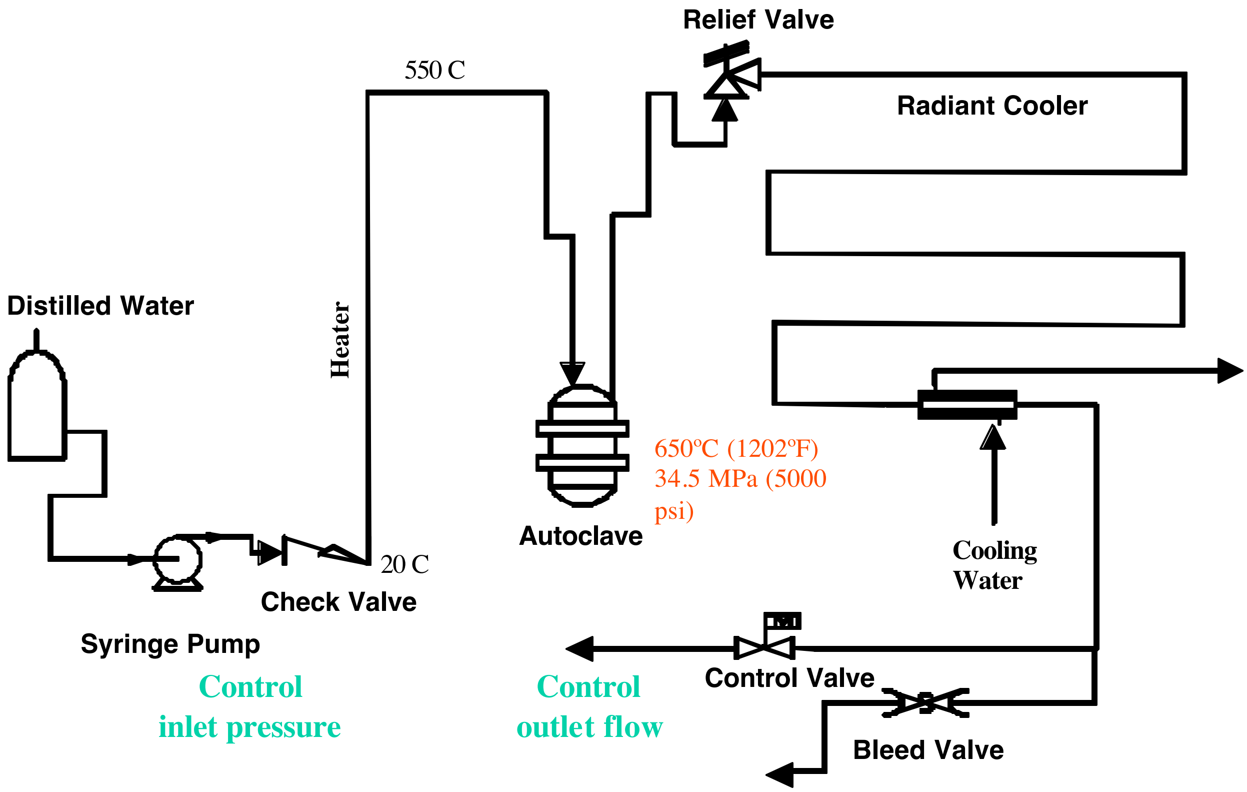

Fig. 3: Design of supercritical steam exposure apparatus.

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